## Field volatility of Dicamba DGA and S-metolachlor

MRID 50958201. Ghebremichael, L., S. Grant, A. Gibbs, M.A.R. Silinski, Report:

and R. Reiss. Dicamba. Off-target Movement Study of Dicamba (A21472E) Tank-Mixed with Roundup PowerMax Herbicide® and Intact<sup>TM</sup> – Northeast

Region of Missouri. Final Report. Unpublished study performed by Syngenta Crop Protection, LLC, Greensboro, North Carolina; Lange

Research and Consulting, Inc (LRC), Fresno, California; RTI International, Research Triangle Park, North Carolina; and Exponent, Inc., Alexandria, Virginia; sponsored by Syngenta Crop Protection, LLC, Greensboro, North Carolina. Report & Task No.: TK0475487. LRC Study No.: LR19453. RTI Study No.: 1271. Exponent Study No.: 1904443.000 - 0521. Study initiation July 2, 2019, and completion January 10, 2020. Experiment initiation July 24, 2019 (completion date not reported; p. 7). Final Report issued January

13, 2020.

MRID 50958201 **Document No.:** 

**Guideline:** OCSPP 835.8100 and 840.1200

**Statements:** The study was completed in compliance with U.S. EPA FIFRA GLP

standards (40 CFR Part 160) with the exception of statistical analysis, test

site information, study weather data, pesticide and crop history, soil

information, test plot preparation and maintenance, and sprayer maintenance (p. 3). Signed and dated Data Confidentiality, GLP Compliance, and Quality Assurance statements were provided (pp. 2-5). An Authenticity Certification

statement was not provided.

**Classification:** This study is acceptable. Monitoring started after the conclusion of

application. An independent laboratory method validation was not

conducted.

128931 (Dicamba DGA) and 108800 (S-metolachlor) PC Code:

**Final EPA** Chuck Peck Signature:

Reviewer: Senior Fate Scientist Date: Final EPA

Frank T. Farruggia, Ph.D. Signature: 2020.10.25 **Reviewer:** Senior Effects Scientist Date: 12:35:27 -04'00'

Signature: Richard Lester CDM/CSS-

**Environmental Scientist** Date: 4/19/20 Dynamac JV

**Reviewers:** Signature: Joan Gaidos **Environmental Scientist** Date: 4/19/20

This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac JV personnel. The CDM/CSS-Dynamac Joint Venture role does not include establishing Agency policies.

2020.10.25

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## **Executive Summary**

Field volatilization of dicamba in Tavium® Plus VaporGrip® Technology herbicide (A21472E, containing dicamba and S-metolachlor) when tank mixed with Roundup PowerMax Herbicide® (glyphosate potassium salt) and Intact<sup>TM</sup> (polyethylene glycol, choline chloride, and guar gum) was examined from a single dicamba- and glyphosate-tolerant soybean plot surrounded by non-dicamba tolerant, glyphosate-tolerant soybeans in Ralls County, Missouri. Vapor sampling and spray drift deposition sampling were conducted for *ca.* 168 hours following application. Dicamba was applied at a nominal rate of 0.5 lbs. a.e./A. The study also examined off-target movement due to volatility and spray drift and resulting impacts to non-target plants. A control plot was established upwind of the test plot for plant effects. No control plot was established for field volatilization measurements.

Air temperatures, surface soil temperatures (i.e., 6 in below surface), and relative humidity the day of application (7/24/19) ranged from 4.34-28.8°C (39.8-83.8°F), 15.9-33.4°C (60.6-92.1°F), and 47-100%, respectively. Air temperatures, surface soil temperatures, and relative humidity ranged from 2.91-31.0°C (37.2-87.8°F), 17.2-35.0°C (63.0-95°F), and 51-100%, respectively, 1 to 7 days after application.

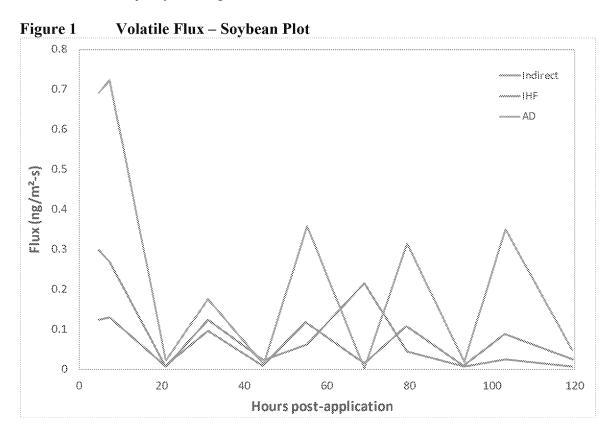
Under field conditions at the test plot, based on calculations using the Indirect method, study authors estimated a peak volatile flux rate of  $0.000298~\mu g/m^2$ ·s accounting for 0.008% of the applied dicamba observed 0 to 4 hours post-application. By the end of the study, study authors estimated a total of 0.046% of dicamba volatilized and was lost from the field. The reviewer confirmed the peak flux rate and estimated that the total of amount of dicamba volatilized and lost from the field by the end of the study was 0.044%. Peak and secondary peak volatile flux rates occurred during the warm daytime hours each day after application.

Under field conditions at the test plot, based on calculations using the Integrated Horizontal Flux method, study authors estimated a peak volatile flux rate of  $0.000216~\mu g/m^2 \cdot s$  accounting for 0.020% of the applied dicamba observed 54.1 to 68.2 hours post-application. By the end of the study, study authors estimated that a total of 0.046% of dicamba volatilized and was lost from the field. The peak volatile flux rate occurred overnight from the second to third day post-application. The secondary peak volatile flux rate occurred during daytime hours the day after application. The reviewer confirmed the peak flux rate and estimated that the total of amount of dicamba volatilized and lost from the field by the end of the study was 0.049%.

Under field conditions at the test plot, based on calculations using the Aerodynamic method, study authors estimated a peak volatile flux rate of  $0.000724~\mu g/m^2$ ·s accounting for 0.012% of the applied dicamba observed 3.8 to 6.4 hours post-application. By the end of the study, study authors estimated that a total of 0.119% of dicamba volatilized and was lost from the field. The reviewer confirmed the peak flux rate and estimated that the total of amount of dicamba volatilized and lost from the field by the end of the study was 0.118%. Peak and secondary peak volatile flux rates occurred during the warm daytime hours each day after application.

Spray drift measurements indicated that dicamba residues were detected above no observed adverse effects concentrations (NOAECs) in only two downwind samples at one hour after

application. Dicamba residues were not detected above the NOAEC in any of the upwind, left wind, or right wind samples. Dicamba residues were detected at a maximum fraction of the amount applied of 0.00134194 in downwind samples. Deposition of dicamba above the NOAEC was detected in the 3 m and 5 m samples from one of the three transects of the downwind direction in the one-hour sampling period. The estimated distance from the edge of the field to reach NOAEC for soybean was 2.8 m (1.3 to 6.0 m for the three transects) in the downwind direction using the reviewer-developed curve. The study authors did not perform fits of spray drift data, determining that they would not be useful due to the low levels of dicamba mass detected in the majority of samples



## Plant effects (50958201, EPA Guideline 850.4150; Supporting files in Appendix 2)

The effect of A21472E (a.i. Dicamba diglycolamine (DGA) salt + a.i. S-Metolachlor) + Roundup PowerMax Herbicide® (a.i. Glyphosate potassium salt) + Adjuvant Intact<sup>TM</sup> on the vegetative vigor of dicot (soybean, *Glycine max*) crops was studied in a spray drift and volatilization study. Nominal test concentrations of Dicamba were 0.50 lb ae/A and Glyphosate were 1.125 lb ae/A. Dicamba test concentrations were analytically confirmed by monitoring field filter collectors during spray application as well as measurement of pre-application and post-application tank solutions; nominal and measured application rates are provided in Table 4. On days 14 and 28 after treatment, the surviving plants along several transects projecting from the treated area were measured for height and visual signs of injury (VSI).

## Spray Drift + Volatility Study

Dicamba-non-tolerant soybean were planted in test plots at distances of approximately 3, 5, 10, 20, 40, 50, 60, and 90 meters from the edge of the treatment application field in the downwind, upwind, and lateral directions. Height effects and visual symptomology were recorded up to 28 days after spray application of the tank mix.

Regression based distances to a 5% reduction in plant height were evaluated for each individual transect. The plant height data from control plots were used to establish the baseline 5% effect level plant height (Table 1). A distance to effect relationship was observed for transects DWB, DWC and SE, however these were shallow responses relative to distance.

Visible symptomology was reported, but the specific phytotoxic symptoms were not. VSI distances were established based on regression estimated distances to a 20% VSI. For the drift + volatility study, three of the downwind transects, two of the left wind transects, and the east diagonal transect showed a dose-response relationship between percent of visual symptoms and distance to the treatment field. Percent of visible symptoms was a maximum of 50% in these fields closest to the treatment field.

Furthest distance to 5% Reduction in Plant Height = 107.4 meters (352.4 feet) Furthest distance to 20% VSI = 39.3 meters (128.9 feet)

## Volatility Study

Dicamba-non-tolerant soybean were planted in test plots at distances of approximately 3, 5, 10, and 20 meters from the edge of the treatment application field in the downwind, upwind, and lateral directions and isolated using plastic sheeting (transect covers) during the application period to prevent exposure to spray drift. Height effects and visual symptomology was recorded up to 28 days after spray application of the tank mix.

When compared to the negative control plot, the reviewer found significant inhibitions in plant height along transect RWB. Heights were uniformly lower than controls for all plots. Visual signs of injury were observed on RWB at a maximum of 10% at 3 m. Similar heights were observed in the RWB spray drift + volatility transect. It is unclear if these reductions are reflecting variability in the field or dicamba related responses. VSI was also observed in RWA, UWA, UWB, LWB, and DWB transects with maximum injury reported as 5%.

Furthest distance to 5% Reduction in Plant Height = <3 meters (<9 feet) Furthest distance to 20% VSI = <3 meters (<9 feet) Table 1. Estimated distances to regulatory threshold responses for reductions in plant

height and visible signs of injury.

Exposure Pathway	Spray Drift + Volatility (uncovered transects)		Volatility (covered transects)		
Transect	Distance to 5% Height (meters)	Distance to 10% VSI (meters)	Distance to 5% Height (meters)	Distance to 10% VSI (meters)	
DWA Drift	>90 <sub>p</sub>	18.0 <sup>a</sup>	<3 b	<3 b	
DWB Drift	107.4 <sup>a</sup>	29.6 <sup>a</sup>	<3 b	<3 b	
DWC Drift	42.7 <sup>a</sup>	39.3 <sup>b</sup>	<3 b	<3 b	
LWA Drift	<3 b	<3 b	<3 b	<3 b	
LWB Drift	<3 b	<5	<3 b	<3 b	
NE Drift	<3 b	<3 b	NA	NA	
NW Drift	<3 b	<3 b	NA	NA	
RWA Drift	119.7 <sup>c</sup>	15.5 <sup>a</sup>	<20 <sup>b</sup>	<3 b	
RWB Drift	105.7 <sup>e</sup>	16.7 <sup>a</sup>	<3 b	<3 b	
SE Drift	67.6 <sup>a</sup>	31.5 <sup>a</sup>	NA	NA	
SW Drift	>90 <sup>b</sup>	<3 b	NA	NA	
UWA Drift	<40 <sup>b</sup>	<3 b	<3 b	<3 b	
UWB Drift	<20 <sup>b</sup>	<3 b	<3 b	<3 b	

<sup>&</sup>lt;sup>a</sup> distance estimated with logistic regression

NA = Not applicable

#### I. Materials and Methods

## A. Materials

1. Test Material

Product Name: A21472E (Tavium® Plus

VaporGrip® Technology; p. 21)

Formulation Type: Capsule suspension

CAS #: 104040-79-1 (dicamba diglycolamine salt)

CAS #: 87392-12-9 (S-metolachlor)

Lot Number: Batch ID 1087560, Other ID HDM9D25081

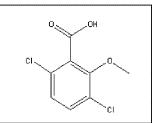
Storage stability: The recertification date of the test substance was

May 31, 2022.

Product Name: Roundup PowerMax® (Glyphosate, (N-

(phosphonomethyl) glycine potassium salt; p. 21)

Formulation type: Not reported CAS Number: Not reported Lot Number: MXZT1109AJ



<sup>&</sup>lt;sup>b</sup> distance estimated visually

<sup>&</sup>lt;sup>c</sup> distance estimated with polynomial regression

Storage stability: The expiration date of the test substance was July 18, 2020.

Product Name: Intact (polyethylene glycol, choline chloride, guar

gum)

Formulation type: Not reported

Lot Number: 0941B047000 (Batch# 374-25)

Storage stability: The expiration date of the test substance was

July 19, 2022.

#### 2. Storage Conditions

The test substance was received by Lange Research and Consulting, Inc. (LRC) on July 2, 2019 and stored ambiently at the LRC facility and at the test site (Appendix I, p. 109). Roundup PowerMax® and Intact<sup>TM</sup> were obtained from commercially available sources and delivered to the site. There were periods when the temperature was above the recommended storage temperature of 86°F, but study authors do not believe it impacted the test substance. Average storage temperature was 80.75°F. The tank mix was prepared, and the test substance sprayed on the test plot on July 24, 2019.

### **B.** Study Design

## 1. Site Description

The test site was located in Ralls County, Missouri, near Perry, Missouri (p. 13). A single soybean plot, measuring ca. 927 ft  $\times$  888.75 ft (283 m  $\times$  271 m, 18.91 A) was treated with a mixture of A21472E (containing dicamba and S-metolachlor), Roundup PowerMax Herbicide® (containing glyphosate potassium salt), and Intact<sup>TM</sup> (polyethylene glycol, choline chloride, and guar gum; p. 21). The soybean plot was planted with dicamba- and glyphosate-tolerant soybeans (Variety: 4119X2) and surrounded by a ca. 300-ft buffer planted in non-dicamba tolerant, glyphosate-tolerant soybeans (Variety: 4268FP). The plot was at least 1,000 feet away from other dicamba applications (Appendix I, p. 110). Soil characterization indicated the USDA textural class was silt loam (Appendix I, p. 127). Dicamba had not been applied to the test plot in the three years preceding the study (Appendix I, Appendix 4, p. 196). Crop history for the three years preceding the study indicated the field had been planted in corn and soybean. Terrain was flat with a slope of 0.63% (p. 22). The test plot was surrounded primarily by agricultural land (Appendix I, Figure 2, p. 170). The test plot and surrounding buffer zone were planted with soybean on June 30, 2019 (Appendix I, p. 107). The soybean seeds were planted at a density of 165,000 seeds/A on 15-inch row spacing for both plantings. The seeds received a proprietary seed treatment, Beck's Escalate, prior to planting.

### 2. Application Details

Application rate(s):

The target application rate was 0.5 lb a.e./A or 15 GPA (p. 12; Appendix I, pp. 117-118). Twelve application monitoring samples consisting of four filter paper samples each were positioned in the

spray area in locations to capture various portions of the spray boom (Appendix I, p. 119).

The spray rate was automatically maintained by variable flow rate technology (Appendix I, p. 119). Actual application pass times were 106.1% of the target application pass time (Appendix I, Table 4, p. 135). Variable flowrate technology ensured sprayer output of 15 GPA.

Irrigation and Water Seal(s): No irrigation or water seals were reported in the study.

Approximately 32 mm of precipitation occurred on July 29, 2019,

five days after application (Appendix I, Table 9, p. 140).

Tarp Applications: Tarps were not used on the test plot. Tarps were used on nine plant

effects transects during application to prevent exposure to spray drift to assess volatile drift exposure only (Appendix I, p. 113).

Tarps were removed immediately after application.

Application Equipment: A self-propelled John Deere 4830 sprayer equipped with a 1,000-

gallon tank, 98.75-ft boom, and 79 Turbo TeeJet® Induction (TTI) 11004 nozzles was used for the spray application (Appendix I, p. 118). The nozzles were installed with 15-inch spacing, and the boom height was set at 20 inches above the crop canopy (~10

inches, 25.4 cm).

**Equipment Calibration** 

Procedures:

Nozzle uniformity was tested by spraying water at a pressure of 63 psi through the boom and measuring nozzle output using SpotOn<sup>®</sup> Model SC-1 sprayer calibrator devices (Appendix I, pp. 118-119). Each nozzle was tested three times to determine variability.

Calibration of the sprayer and nozzles established the total boom output per minute of spray to be 151.87 LPM (liters per minute).

Application Regime: The application rates and methods used in the study are

summarized in Table 2.

Table 2. Summary of application methods and rates for dicamba

Field	Application Method	Time of Application (Date and Start Time)	Amount Dicamba Applied <sup>1</sup> (lbs)	Area Treated (acres)	Calculated Application Rate <sup>2</sup> (lb ae/acre)	Reported Application Rate (gal/acre)
Soybean	Spray	7/24/2019 at 10:50	9.46	18.91	0.5	15

Data obtained from Appendix I, pp. 112, 118, 126 and Appendix I, Table 5, p. 136 of the study report.

Application Scheduling: Critical events of the study in relation to the application period are

provided in Table 3.

<sup>&</sup>lt;sup>1</sup> Reviewer calculated as application rate (lb a.e./acre)  $\times$  area treated (acres).

<sup>&</sup>lt;sup>2</sup> The target application rate of 0.5 a.e./acre is reported. The study does not calculate an actual application rate.

Table 3. Summary of dicamba application and monitoring schedule

Field	Treated Acres	Application Period	Initial Air/Flux Monitoring Period <sup>1</sup>	Water Sealing Period	Tarp Covering Period
		7/24/2019	7/24/2019		7/24/2019
Soybean	18.91	between	between	Not Applicable	between
		10:50 - 11:10	11:26 – 15:22		10:50 - 11:10

Data obtained from Appendix I, p. 112; Appendix I, Table 5, p. 136; and Appendix III, Table 2, p. 370 of the study report.

## 3. Soil Properties

Soil properties measured before the study are provided in **Table 4**. pH of the soil was 5.4 (Appendix I, Appendix 3, p. 193). Soybean plants were at the V4 growth stage.

Table 4. Summary of soil properties for the soybean plot

Field	Sampling Depth (inches)	USDA Soil Textural Classification	USGS Soil Series	WRB Soil Taxonomic Classification	Bulk Density (g/cm³)	Soil Composition
Soybean	0-6	Silt Loam	Putnam silt loam and Mexico silt loam	Not Reported	1.04	% Organic Carbon <sup>1</sup> = 1.45% % Sand = 14% % Silt = 65% % Clay = 21%

Data obtained from Appendix I, pp. 111, 127 and Appendix I, Appendices 2-3, pp. 189-193 of the study report.  $^{1}$ Reviewer calculated as: organic carbon (%) = organic matter (%)/1.72. Organic matter was reported as 2.5%.

Figures 2 and 3 are plots of soil temperature and soil moisture measured throughout the study.

<sup>&</sup>lt;sup>1</sup> Initial air monitoring period is that for perimeter stations. The initial period at the center station was 7/24/2019 between 11:32 - 15:23 (Appendix III, Table 4, p. 374).

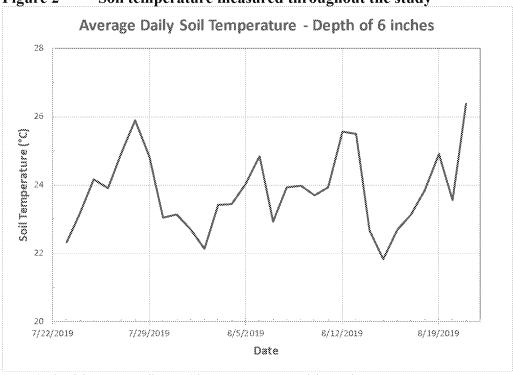
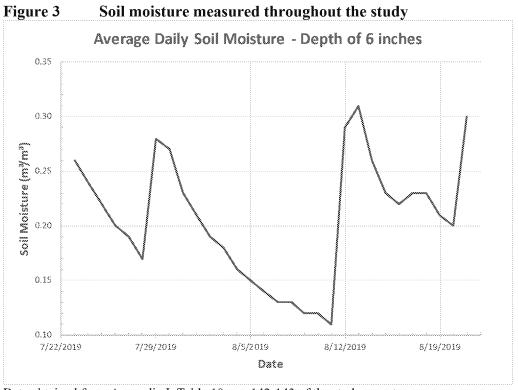


Figure 2 Soil temperature measured throughout the study

Data obtained from Appendix I, Table 10, pp. 142-143 of the study report.



Data obtained from Appendix I, Table 10, pp. 142-143 of the study report.

#### 4. Source Water

The source of the tank mix water was a rural surface water supply. The pH of the tank mix water was 8.2 as measured at the analytical laboratory, an alkalinity of 99 mg CaCO<sub>3</sub>/L, and a conductivity of 0.38 mmhos/cm.

## 5. Meteorological Sampling

Five meteorological stations were used to collect weather data during the study (Appendix I, p. 115).

The 10-meter main meteorological station was located upwind *ca.* 44 feet north of the test plot (Appendix I, pp. 114-115). The system included a Campbell CR1000X Datalogger and a Campbell Scientific 4G Cellular Modem to remotely monitor data. The station included sensors for monitoring windspeed and direction (a 3D anemometer and two 2D anemometers), air temperature, relative humidity, solar radiation, and precipitation. Windspeed and direction, air temperature, and relative humidity were reported at heights of 1.7, 5, and 10 m above the ground. Solar radiation and precipitation were reported at the ground surface (Appendix III, Table 1, p. 366).

A boom height anemometer collected wind speed and wind direction data *ca.* 10 feet downwind of the treated plot south edge during application at a height of 20 inches above the crop canopy (Appendix I, pp. 114-115). The sensor measured every second and summarized results every one minute and every two minutes.

The long duration main meteorological station was located outside of the application area *ca.* 10 feet north of the treated area border and recorded data for 28 days post-test substance application (Appendix I, pp. 114, 116). The station included one Campbell Scientific ClimaVUE sensor which measured wind speed and direction, air temperature, relative humidity, solar radiation, precipitation, and barometric pressure. The sensor was located at a height of 1.5 m. A Campbell Scientific soil moisture/temperature sensor measured soil moisture and soil temperature at a depth of 6 inches (Appendix I, Table 10, pp. 142-143).

The primary flux meteorological station was deployed outside of the plot prior to application and was then moved to the center of the plot, remaining there until after the final drift sample was collected on the morning of July 31, 2019 (Appendix I, p. 116). The station included a Campbell CR1000X Datalogger and a Campbell Scientific 4G Cellular Modem to remotely monitor data. The station included sensors for air temperature, wind speed, and wind direction at heights of 0.15, 0.33, 0.55, 0.9, and 1.5 m above the crop canopy.

A secondary flux meteorological station also recorded air temperature, wind speed, and wind direction at heights of 0.15, 0.33, 0.55, 0.9, and 1.5 m above the canopy (Appendix I, p. 116). The secondary meteorological station was positioned upwind and outside of the sprayed area.

Details of the sensor heights and the meteorological parameters for which data were collected are illustrated in **Table 5**. The location of the meteorological equipment is shown in **Attachment 3**.

Table 5. Summary of meteorological parameters measured in the field

Field	Minimum Fetch (m)	Parameter	Monitoring heights	Averaging Period	
		Air temperature	1.7.5 and 10 m		
Soybean		Relative humidity	1.7, 5, and 10 m above ground surface		
10-Meter Main	Not Reported	Wind speed/wind direction	above ground surface	1 minute	
Met. Station	-	Precipitation	C1C		
		Solar radiation	Ground surface		
Soybean Boom Height Anemometer	Not Reported	Wind speed/wind direction	20 in. above canopy	1 minute and 2 minutes	
		Air temperature			
	Not Reported	Relative humidity			
Soybean		Wind speed/wind direction	1.5 m above ground	Not Reported	
Long Duration		Precipitation	surface		
Main Met.		Solar radiation			
Station		Barometric pressure			
		Soil temperature	6 in aleas danth	Not Donoutod	
		Soil moisture	6 inches depth	Not Reported	
Soybean		Air temperature	0.15, 0.33, 0.55, 0.9, and		
Primary Flux Met. Station	Not Reported	Wind speed/wind direction	1.5 m above canopy <sup>1</sup>	1 minute	
Soybean		Air temperature	0.15, 0.33, 0.55, 0.9, and		
Secondary Flux Met. Station	Not Reported	Wind speed/wind direction	1.5 m above canopy <sup>1</sup>	1 minute	

Data obtained from Appendix I, pp. 112, 115-116, Appendix III, pp. 365-366.

#### 6. Air Sampling

Two pre-application samples were collected at 0.15 m and 0.33 m above the crop canopy at the approximate center of the test plot (Appendix I, p. 120). Samples were collected for *ca.* 6 hours on July 23, 2019.

Post-application in-field air samplers were used for flux monitoring for *ca.* 168 hours following application (Appendix I, p. 120). Samplers were placed on a mast in the approximate center of the plot directly following spray application at heights of 0.15, 0.33, 0.55, 0.90, and two at 1.5 m above the crop canopy. Samples were collected at *ca.* 6, 12, 24, 36, 48, 60, 72, 84, 96, 108, 120, 132, 144, 156, and 168 hours post-application. The 0 to 6-hour and 6 to 12-hour samples were pro-rated based on the time remaining until sunset on the day of application, with subsequent samples being collected on a morning (after sunrise)-evening (prior to sunset) schedule.

Off the plot, eight perimeter air monitoring stations were located 1.5 m above the crop canopy and 10 m outside the edge of the plot (Appendix I, pp. 120-121). Samples were collected at *ca.* 1, 6, 12, 24, 36, 48, 60, 72, 84, 96, 108, 120, 132, 144, 156, and 168 hours post-application. The 0 to 6-hour and 6 to 12-hour samples were pro-rated based on the time remaining until sunset on the day of application, with subsequent samples being collected on a morning (after sunrise)-evening (prior to sunset) schedule.

<sup>&</sup>lt;sup>1</sup> These heights above the canopy are equivalent to 0.4, 0.58, 0.8, 1.15, and 1.75 m above ground level.

## 7. Spray Drift Monitoring

The spray drift test system consisted of three downwind transects, two left wind transects, two right wind transects, and two upwind transects. All transects were perpendicular to the edge of the field. Deposition collectors (Whatman #1 15 cm diameter filter papers) were placed on all transects at the following distances from the edge of the spray area: 3, 5, 10, 20, 40, 50, and 60 m. Deposition collectors were also placed at 90 m in the downwind transects only. Deposition collectors were secured to carboard squares and attached to a horizontal plastic platform at crop height (~10 in, 25.4 cm). Initial deposition samples were collected 30 minutes to 1 hour after spray application was completed. Deposition samples were collected at intervals of 1, 24, 48, 72, 96, 120, 144, and 168 hours post-application (Appendix I, p. 121).

#### 8. Plant Effects Monitoring

The off-target movement of dicamba due to spray drift and volatility following the application of dicamba to dicamba-tolerant soybeans was assessed by comparing plant heights and visual plant symptomology along transects of non-tolerant soybean crop surrounding the tolerant soybean field and perpendicular to the sprayed field edges of the application area, as well as four transects radiating from the corners of the sprayed field (Figure 2, p. 79). Dicamba-non-tolerant soybean were evaluated at distances of approximately 3, 5, 10, 20, 40, 50, and 60 meters from the edge of the treatment application field, with an additional filter paper sample was placed approximately 90 m from the application area for the three downwind transects only. Transects were not located within pre-determined designated ingress and egress areas for the sprayer. Along with the plant effect transects located immediately adjacent to the treated field, four upwind control areas were identified and evaluated for plant height.

Plant effects from volatility were assessed by isolating a portion of the non-tolerant soybean crop immediately adjacent to the treated areas using plastic sheeting (transect covers) during the application period to prevent exposure to spray drift (Figure 2, p. 79). The non-tolerant soybeans that were covered during the application were used to assess effects to plant height and visual symptomology from dicamba volatility. The plastic covers were intended to remain in place for approximately 30 min post-application before permanent removal for the remainder of the study. Transects for volatility only were 20 m long and plant height measurements and visual symptomology ratings were completed at approximately 3, 5, 10, and 20 m from the sprayed area at 0, 14, and 28 days after treatment.

At each distance along each transect, ten plants were selected non-systematically with no attempt to measure the same plant at the subsequent time points. Plant height was measured by holding a plant upright and measuring the distance between the ground and the tip of the most recently emerged apical bud to the nearest centimeter using a metal metric ruler. Where multiple shoots were present, measurements along the main shoot were taken.

### 9. Sample Handling and Storage Stability

PUF sorbent tube and deposition filter paper samples were handled with clean nitrile gloves, which were replaced after the collection of samples and prior to installation of a new sample

media for the next sampling interval (Appendix I, pp. 124-125). PUF sorbent tubes and filter papers were placed in pre-labeled conical tubes. Field volatility, spray drift, application monitoring, field exposed spikes, and transit samples were kept in frozen storage (coolers containing dry ice) prior to and during shipment to the analytical test site. Pre-application, application verification (in-swath), post-application, field exposed spikes, and transit stability PUF samples were stored in freezers prior to shipment, with the preapplication and application verification samples stored in separate freezers from the post application, field exposed spikes, and transit stability samples. Samples were shipped in ice chests containing dry ice via FedEx to the analytical test site. Soil (ambient) and water samples (cool on blue ice) were shipped to the analytical laboratory by FedEx.

All field collected PUF and filter paper samples were extracted within 35 and 50 days, respectively, after collection (p. 31). All field exposed QC and transit stability samples were extracted within 76 days after fortification. Freezer storage studies were conducted previously (MRIDs 50102117 and 50102118) demonstrating storage stability of at least 90 and 115 days for PUF and filter paper samples, respectively.

## 10. Analytical Methodology

- Sampling Procedure and Trapping Material: Flux monitoring equipment consisted of polyurethane foam (PUF) sampling tubes (SKC Cat. No. 226 92) and SKC® air sampling pumps (Model Nos. 224-44XR, 224-43XR, 224-PCXR3, 224-PCXR4, and 224-PCXR7; Appendix I, p. 120). The pumps were powered by 12 volt batteries and protected from precipitation by ¾ inch diameter PVC pipes and plastic bags. Pumps were calibrated to a flow rate of 3.0 L/min.
- Extraction method: PUF samplers were extracted and analyzed using Monsanto method ME-1902-02 (p. 28, Appendix II, p. 282). The contents of the PUF sorbent tubes were extracted using methanol containing stable-labeled internal standard. The sample was fortified with 0.1 mL of internal standard, and a 7/16″ grinding ball and 29.8 mL of methanol were added. The sample tubes were capped and agitated on a SPEX Geno/Grinder at 1200 rpm for 30 minutes. A 1.8 mL aliquot was filtered using a 0.2 μm polytetrafluoroethylene (PTFE) filter plate, evaporated to dryness under nitrogen at 50°C, and reconstituted with 0.36 mL of 25% methanol in water. The sample was vortexed and analyzed by LC-MS/MS with electrospray ionization in negative ion mode.

Filter paper samplers were extracted and analyzed using Monsanto method ME-1871-01 (p. 28, Appendix II, p. 286). The filter paper samples were extracted using methanol containing stable-labeled internal standard. The sample was fortified with 0.1 mL of internal standard, and a 7/16" grinding ball and 30 mL of 25% methanol were added. The sample tubes were capped and agitated on a SPEX Geno/Grinder at 1200 rpm for 5 minutes. The tubes were centrifuged at 4500 relative centrifugal force (rcf) for 5 min at ~10 °C, and a 0.35-mL aliquot of supernatant was filtered (0.2  $\mu$ m hydrophilic polypropylene [GHP] filter plate) into a sample plate with glass inserts for analysis by LC-MS/MS with electrospray ionization in negative ion mode.

• Method validation (Including LOD and LOQ): Method validation was achieved by fortifying three samples each at fortification levels of 1 ng/PUF, 3 ng/PUF, and 30 ng/PUF (p. 16; Appendix II, pp. 300). Validation assessments showed acceptable accuracy between 70% and 120% and precision (<20% RSD) for all fortified matrices at each fortification level. The mean overall recovery of the nine fortification samples for the primary ion transition was 84.3%. Mean recoveries for the primary ion transition were 90.4%, 84.3%, and 78.2%, for the fortification levels of 1 ng/PUF, 3 ng/PUF, and 30 ng/PUF, respectively, with RSD's ≤6.9%. The mean overall recovery for the secondary ion transition was 101% (Appendix II, Table 1, p. 300). Mean recoveries for the secondary ion transition were 95.2%, 107%, and 99.4%, for the fortification levels of 1 ng/PUF, 3 ng/PUF, and 30 ng/PUF, respectively, with RSD's ≤10.3%. No independent laboratory validation is provided. The LOD was 0.297 ng/PUF and the LOQ was 0.995 ng/PUF. During the study, the LOQ was 1 ng/PUF.

Method validation was achieved by fortifying three samples each at fortification levels of 0.005 µg/filter paper, 0.05 µg/filter paper, and 0.5 µg/filter paper (p. 16, Appendix II, pp. 312). Validation assessments showed acceptable accuracy between 70% and 120% and precision (<20% RSD) for all fortified matrices at each fortification level. The mean overall recovery of the nine fortification samples was 107%. Mean recoveries were 102%, 110%, and 110% for fortification levels of 0.005 µg/filter paper, 0.05 µg/filter paper, and 0.5 µg/filter paper, respectively, with RSD's  $\leq$  5.4%. No independent laboratory validation is provided. The LOD was 0.00149 µg/filter paper and the LOQ was 0.00497 µg/filter paper. During the study, the LOQ was 0.005 µg/filter paper.

• Instrument performance: Calibration standards were prepared at concentrations ranging from 0.15 to 75 ng/PUF (Appendix II, p. 281). Concentrations were 0.15, 0.225, 0.3, 0.75, 1.5, 2.25, 3, 7.5, 15, 22.5, 30, and 75 ng/PUF. Analyst software was used to derive the calibration curve using a weighted linear curve (1/x<sup>2</sup>; Appendix II, pp. 283-284).

Calibration standards were prepared at concentrations ranging from 0.0015 to 6  $\mu$ g/filter paper (Appendix II, p. 285). Concentrations were 0.0015, 0.003, 0.0075, 0.015, 0.03, 0.075, 0.15, 0.3, 0.75, 1.5, 3, and 6  $\mu$ g/filter paper. Analyst® software was used to derive the calibration curve using a weighted linear curve (1/ $x^2$ ; Appendix II, pp. 288).

## 11. Quality Control for Air Sampling

Lab Recovery: 28 of 48 laboratory spike recoveries are within the acceptable range of

90-110% (Appendix II, Table 4, p. 303). All laboratory spike recoveries are within the range of 76-127%. Laboratory spike samples were

prepared at fortification levels of 1 ng/PUF (24 samples) and 30 ng/PUF (24 samples). Average recoveries were 98.0% and 107% at 1 ng/PUF and

30 ng/PUF, respectively.

Field blanks: Two six-hour pre-application samples were collected from the center of

the test plot on July 23, 2019, the day before application (Appendix I, p.

120). Dicamba was not detected in either pre-application sample

(Appendix II, Table 6, p. 305).

All six control samples from field spike analyses also contained no detectable dicamba (Appendix II, Table 2, p. 301).

Field Recovery: Nine 6-hour and nine 12-hour field spike samples were collected at

concentration levels of 3, 10, and 30 ng/PUF. A total of six field spikes were prepared at each concentration level. Most field spike recoveries are within the acceptable range with overall recoveries of 95.3% to 113% at 3 ng/PUF, 97.5% to 117% at 10 ng/PUF, and 84.9% to 128% at 30 ng/PUF (Appendix II, p. 293 and Appendix II, Table 2, p. 301).

Travel Recovery: Two sets of three transit stability PUF samples were fortified at 3 and 30

ng/PUF, stored, and shipped frozen up to 37 days (Appendix II, p. 293). The range of recoveries from the fortified samples was from 98% to 114% at 3 ng/PUF and 105% to 117% at 30 ng/PUF (Appendix II, Table

3, p. 302).

Breakthrough: Laboratory spike samples that were fortified at 30 ng/PUF had recoveries

ranging from 85.6% to 127% (Appendix II, Table 4, p. 303). The highest dicamba amount measured on a PUF sample (excluding laboratory and field spikes) was 15.7 ng/PUF (Appendix II, Tables 6-7, pp. 305-311) which is *ca.* 52% of the highest fortification level, indicating that

dicamba loss due to breakthrough is unlikely.

## 12. Quality Control for Deposition Sampling

Lab Recovery: 23 of 48 laboratory spike recoveries are within the acceptable range of

90-110%. All laboratory spike recoveries are within the range of 80-118%. Laboratory spike samples were prepared at fortification levels of 0.005 µg/filter (24 samples) and 0.5 µg/filter (24 samples). Average recoveries were 105% and 111% at 0.005 µg/filter and 0.5 µg/filter, respectively. Control samples from the field spike analysis did not

contain detectable levels of dicamba (Appendix II, p. 314).

Travel Recovery: Ten transit stability filter paper samples were fortified at 0.01 and 0.05

μg/filter paper and placed on dry ice (Appendix II, p. 313). The range of

recoveries from the fortified samples was from 106% to 118%.

### 13. Application Verification

Twelve application monitoring samples consisting of four filter paper samples each were positioned in the spray area in locations to capture various portions of the spray boom (Appendix I, p. 119). The mean recovery relative to the target was 92.3% (Appendix II, p. 296).

Variable flow rate technology was used to adjust sprayer output ensuring sprayer output at the target rate of 15.0 GPA (Appendix I, p. 119). Pass times were not used to calculate an application rate.

Tank mix samples were also collected and analyzed to verify the amount of dicamba present in the tank mix (Appendix I, p. 119).

### 14. Deposition and Air Concentration Modeling

Off-target air concentrations and deposition were calculated for the test plot based on the calculated flux rates and relevant meteorological data. U.S. EPA's AERMOD model (version 19191) was used to estimate air concentrations and deposition (Appendix III, pp. 362-363). A second set of air concentration estimates was made for a hypothetical 200-acre application using the Probabilistic Exposure and Risk model for Fumigants (PERFUM, version 3). PERFUM modeling was performed using three different meteorological data sets, from Raleigh, North Carolina; Peoria, Illinois; and Lubbock, Texas.

The reviewer chose the maximum flux predicted by any method for each period to represent that period. Periods were then mapped onto hours of the day (1-24), where the maximum flux rate for each hour was then chosen to represent that hour, regardless of the day from which it was collected. In cases where two periods occurred in a single hour, a weighted average of the flux rates was used. The 24-hour flux profile for the first two days were used as inputs for PERFUM and the average flux rate and as adjustment factors for input into AERMOD. The study authors used the flux rates from the Indirect method, so they were slightly different from those the reviewer used. However, the differences in flux rates did not impact the overall modeling conclusions.

Air concentration, dry deposition, and wet deposition estimates were made at distances from the field every 5 m from 5 to 90 m using AERMOD (Appendix III, pp. 377-378). The flux obtained using the aerodynamic method was used in the modeling. The maximum 24-hour dry deposition at a distance of 5 m ranged from 0.591 to  $1.169 \,\mu\text{g/m}^2$  (Appendix III, Table 7, p. 381).

PERFUM modeling calculated off-target air concentrations for a 200-acre field based on historical meteorological data (Appendix III, pp. 363, 382). Modeled dicamba air concentrations were calculated at distances of 5, 10, 25, 50, and 90 m from the field. Modeled 95<sup>th</sup> percentile 24-hour air concentrations ranged from 2.3 to 5.9 ng/m³ at 5 m from the edge of the treated field and 1.0 to 3.6 ng/m³ at 90 m from the edge of the field.

The reviewer was able to confirm the modeling conclusions both for deposition and air concentrations, although the reviewer estimated deposition and air concentration values were slightly higher (1.6-2.35 µg/m² and 6-10 ng/m³) based on a higher flux rate during the evening hours. The reviewer also conducted modeling analysis for Little Rock, Arkansas, Nashville, Tennessee, and Springfield, Missouri, attempting to capture modeling results representative of soybean growing regions in Arkansas, Tennessee, and Missouri. Modeled 95<sup>th</sup> percentile 24-hour air concentrations were slightly higher (9-19 ng/m³), but comparable, than those achieved for the North Carolina, Illinois, and Texas modeling results.

#### II. Results and Discussion

## A. Empirical Flux Determination Method Description and Applicability

#### Indirect Method

The indirect method, commonly referred to as the "back calculation" method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the indirect method, air samples are collected at various locations outside the boundaries of a treated field. Meteorological conditions, including air temperature, wind speed, and wind direction, are also collected for the duration of the sampling event. The dimensions and orientation of the treated field, the location of the samplers, and the meteorological information are used in combination with the AERMOD dispersion model (Version 18081) and a unit flux rate of 0.001 g/m<sup>2</sup>·s to estimate concentrations at the sampler locations. Since there is a linear relationship between flux and the concentration at a given location, the results from the AERMOD model runs are compared to those concentrations actually measured, and a regression is performed, using the modeled values along the x-axis and the measured values along the yaxis. If the linear regression does not result in a statistically significant relationship, the regression may be rerun forcing the intercept through the origin, or the ratio of averages between the monitored to modeled concentrations may be computed, removing the spatial relationship of the concentrations. The indirect method flux back calculation procedure is described in detail in Johnson et al., 1999.

Study authors used a similar analysis to obtain flux rates. Initially a linear regression analysis was conducted by forcing the intercept through zero and the slope was used to estimate the flux rate. If the slope was not significant, the spatial relationship was removed by sorting both the measured and modeled air concentrations (independently) in ascending order, then redoing the regression, with the final flux estimate calculated as the slope of this alternative regression multiplied by the nominal flux.

### Aerodynamic Method

The aerodynamic method, also referred to as the "flux-gradient" method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the aerodynamic method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from 0.5 to 10 feet. Likewise, temperature and wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. These relationships are then incorporated into an equation to estimate flux. The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the aerodynamic method is Thornthwaite-Holzman Equation, which is shown in the following expression:

Equation 1 
$$P = \frac{k^2 (\Delta \overline{c})(\Delta \overline{u})}{\phi_m \phi_p \left[\ln \left(\frac{z_2}{z_1}\right)\right]^2}$$

where P is the flux in units of  $\mu g/m^2 \cdot s$ , k is the von Karman's constant (dimensionless  $\sim 0.4$ ),  $\Delta c$  is the vertical gradient pesticide residue concentration in air in units of  $\mu g/m^3$  between heights  $z_{top}$  and  $z_{bottom}$  in units of meters,  $\Delta \bar{u}$  is the vertical gradient wind speed in units of m/s between heights  $z_{top}$  and  $z_{bottom}$ , and  $\phi_m$  and  $\phi_p$  are the momentum and vapor stability correction terms respectively. Following the conditions expected in the neutrally stable internal boundary layer characterized by an absence of convective (buoyant) mixing but mechanical mixing due to wind shear and frictional drag, a log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. The adjusted values of the concentration, temperature, and wind speed from this regression is incorporated into Equation 1 to arrive at Equation 2 which is ultimately used to compute the flux.

Equation 2 
$$Flux = \frac{-(0.42)^{2} (c_{ztop} - c_{zbottom})(u_{ztop} - u_{zbottom})}{\phi_{m} \phi_{p} \ln \left(\frac{z_{top}}{z_{bottom}}\right)^{2}}$$

where  $\phi_m$  and  $\phi_p$  are internal boundary layer (IBL)stability correction terms determined according to the following conditions based on the calculation of the Richardson number,  $R_i$ :

Equation 3 
$$R_{i} = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\frac{T_{ztop} + T_{zbottom}}{2}\right) + 273.16\right] + \left(u_{ztop} - u_{zbottom}\right)^{2}}$$

where  $T_{ztop}$  and  $T_{zbottom}$  are the regressed temperatures at the top and bottom of the vertical profile in units of  ${}^{\circ}C$ .

if R<sub>i</sub> >0 (for Stagnant/Stable IBL)  

$$\phi_m = (1+16R_i)^{0.33}$$
 and  $\phi_p = 0.885(1+34R_i)^{0.4}$ 

if R<sub>i</sub> <0 (for Convective/Unstable IBL) 
$$\phi_m = (1-16R_i)^{-0.33}$$
 and  $\phi_p = 0.885(1-22R_i)^{-0.4}$ 

The minimum fetch requirement that the fetch is 100 times the highest height of the air sampler for this method to be valid was not satisfied at for any of the sampling periods. Average fetch distances ranged from 140 to 166 m, while the minimum fetch distance was 175 m (the highest height of the samplers was 1.75 m, 1.5 m above the crop canopy of 0.25 m). As a result, there is some uncertainty in whether the plume was completely captured and in the resulting flux rates. The aerodynamic method used to estimate flux and related equations are presented in Majewski et al., 1990.

### Integrated Horizontal Flux Method

The integrated horizontal flux method, also referred to as the "mass balance" method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the integrated horizontal flux method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights,

ranging from approximately 0.5 to 5 feet. Likewise, wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the air concentration and wind speed following the log law relationships for the atmospheric boundary layer. These relationships are then incorporated into an equation to estimate flux. The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the integrated horizontal flux method is the following expression:

Equation 4 
$$P = \frac{1}{x} \int_{z_0}^{z_p} \overline{c} \overline{u} dz$$

where P is the volatile flux in units of  $\mu g/m^2 \cdot s$ , c is the average pesticide residue concentration in units of  $\mu g/m^3$  at height Z in units of meters, u is the wind speed in units of m/s at height Z, x is the fetch of the air trajectory blowing across the field in units of meters,  $Z_0$  is the aerodynamic surface roughness length in units of meters,  $Z_p$  is the height of the plume top in units of meters, and dz is the depth of an incremental layer in units of meters. Following trapezoidal integration, equation 3 is simplified as follows in equation 5 (Yates, 1996):

Equation 5 
$$P = \frac{1}{x} \sum_{Z_0}^{Z_p} (A * Ln(z) + B) * (C * Ln(z) + D) dz$$

where A is the slope of the wind speed regression line by ln(z), B is the intercept of the wind speed regression line by ln(z), C is the slope of the concentration regression by ln(z), D is the intercept of the concentration regression by ln(z), z is the height above ground level.  $Z_p$  can be determined from the following equation:

Equation 6 
$$Z_P = \exp\left[\frac{(0.1 - D)}{C}\right]$$

The minimum fetch requirement of 20 meters for this method to be valid was satisfied at all times. The surface roughness length was below the maximum surface roughness requirement of 0.1 meters for only the first monitoring period. The surface roughness length for the remaining monitoring periods ranged from 0.11 to 0.19, adding uncertainty to the flux rates that were estimated.

#### **B.** Temporal Flux Profile

The flux determined from the registrant and reviewer for each sampling period after the application is provided in **Tables 6** and **7**. The pH of the tank mix was 4.9 before and after the application.

Table 6. Field volatilization flux rates of dicamba obtained in study - Indirect Method

Sampling	Date/	Sampling	Flux Estimate				
Period	Time	Duration (hours)	Reviewer (µg/m²·s)	Notos		Notes	
1	7/24/19 11:26 – 15:22	3.93	0.000287	Regression	0.000298	A	
2	7/24/19 15:24 – 18:03	2.65	0.000250	Regression	0.000270	A	
3	7/24/19-7/25/19 18:08 – 7:40	13.53	0.000006	Regression, no intercept	0.000010	В	
4	7/25/19 7:44 – 18:02	10.30	0.000096	Regression, no intercept	0.000096	A	
5	7/25/19-7/26/19 18:07 – 7:16	13.15	0.000009	Regression, no intercept	0.000009	A	
6	7/26/19 7:19 – 17:39	10.33	0.000119	Regression, no intercept	0.000119	A	
7	7/26/19-7/27/19 17:42 – 7:45	14.05	0.000007	Regression	0.000015	A	
8	7/27/19 7:47 – 18:03	10.27	0.000108	Regression, no intercept	0.000108	A	
9	7/27/19-7/28/19 18:08 – 7:50	13.70	0.000009	Regression, no intercept	0.000009	A	
10	7/28/19 7:52 – 17:52	10.00	0.000088	Regression, no intercept	0.000088	A	
11	7/28/19-7/29/19 17:55 – 10:14	16.32	0.000021	Regression	0.000026	A	
12	7/29/19 10:18 – 18:02	7.73	NC	С	NC	С	
13	7/29/19-7/30/19 18:08 – 7:50	13.70	NC	С	NC	С	
14	7/30/19 7:53 – 18:03	10.17	NC	С	NC	С	
15	7/30/19-7/31-19 18:06 – 7:48	13.70	NC	С	NC	С	

Data obtained from Appendix III, Table 2-3, pp. 370-371 of the study report.

NC indicates not calculated.

 $Sample\ durations\ calculated\ by\ reviewer\ in\ 128931\_50958201\_DER-FATE\_835.8100\_4-16-20\_Calc.xlsx.$ 

#### Notes

- A Flux calculated using a regression with the intercept going through 0
- B Flux calculated by sorting both measured and modeled concentrations in descending order and conducting regression
- C Flux was not calculated for Periods 12-15 because dicamba mass in the PUF tubes was below LOD.

Table 7. Field volatilization flux rates of dicamba obtained in study – Integrated Horizontal

Flux and Aerodynamic Methods

	•		Flux Estimate				
Sampling Period	Date/ Time	Sampling Duration (hours)	Reviewer (µg/m²·s)	Registrant (µg/m²·s)	Empirical Flux Determination Method*	Notes	
1	7/24/19 11:32 – 15:23	3.8	0.000129 0.000683	0.000124 0.000692	IHF AD		
2	7/24/19 15:28 – 18:04	2.6	0.000141 0.000718	0.000131 0.000724	IHF AD		
3	7/24/19-7/25/19 18:09 – 7:41	13.5	0.000011 0.000023	0.000008 0.000024	IHF AD		
4	7/25/19 7:44 – 18:03	10.3	0.000129 0.000171	0.000125 0.000175	IHF AD		
5	7/25/19-7/26/19 18:07 – 7:21	13.2	0.000027 0.000014	0.000024 0.000013	IHF AD		
6	7/26/19 7:23 – 17:58	10.6	0.000070 0.000356	0.000062 0.000359	IHF AD		
7	7/26/19-7/27/19 17:39 – 7:47	14.1	0.000219 0.000003	0.000216 0.000003	IHF AD		
8	7/27/19 7:51 – 18:15	10.4	0.000051 0.000312	0.000045 0.000314	IHF AD		
9	7/27/19-7/28/19 18:23 – 7:55	13.5	0.000009 0.000021	0.000007 0.000020	IHF AD		
10	7/28/19 7:57 – 17:56	10.0	0.000034 0.000349	0.000026 0.000351	IHF AD		
11	7/28/19-7/29/19 18:01 – 10:11	16.2	0.000009 0.000050	0.000007 0.000049	IHF AD		
12	7/29/19 10:13 – 18:05	7.9	NC NC	NC NC	IHF AD	A	
13	7/29/19-7/30/19 18:10 – 7:54	13.7	NC NC	NC NC	IHF AD	A	
14	7/30/19 7:57 – 18:05	10.1	NC NC	NC NC	IHF AD	A	
15	7/30/19-7/31-19 18:09 – 7:54	13.7	NC NC	NC NC	IHF AD	A	

Data obtained from Appendix III, Table 4, p. 374 of the study report.

Dicamba was not detected in the PUF tubes for periods 12-15; hence, no flux was calculated for those periods (Appendix III, Tables 3-4, pp. 371, 374).

Using the indirect method, study authors estimated the maximum flux rate (0.000298  $\mu g/m^2 \cdot s$ ) to occur during the initial sampling period after application (Appendix III, Table 3, p. 371).

NC indicates not calculated.

<sup>\*</sup>Methods legend: AD = Aerodynamic Method, IHF = Integrated Horizontal Flux. Notes

A Flux was not calculated for Periods 12-15 because dicamba mass in the PUF tubes was below LOD.

Using the aerodynamic method, study authors estimated the maximum flux rate (0.000724  $\mu g/m^2 \cdot s$ ) to occur during the second period after application (Appendix III, Table 4, p. 374). Using the integrated horizontal flux method, study authors estimated the maximum flux (0.000216  $\mu g/m^2 \cdot s$ ) to occur during period 7, the nighttime hours *ca.* 54.1 to 68.2 hours after application. It should be noted that during this time period, the regression of concentrations with height had a low r-squared value (0.53). In general, reviewer estimated flux rates matched those derived by the study authors.

R-squared values for the linear regressions of modeled and measured air concentrations in the indirect method ranged from 0.617 to 0.977 (Appendix III, p. 392). The lowest R-squared value was 0.617 for period 7. All other R-squared values were  $\geq$  0.851.

R-squared values in log-linear vertical profiles of wind speed for the integrated horizontal flux and aerodynamic methods were all greater than 0.98. R-squared values in log-linear vertical profiles of concentration for the integrated horizontal flux and aerodynamic methods were all greater than 0.94 except for Periods 5 (0.73) and 7 (0.54). R-squared values in log-linear vertical profiles of temperature for the aerodynamic method were all greater than 0.74 except for Periods 2 (0.40), 4 (0.49), 6 (0.66), and 10 (0.62).

## C. Spray Drift Measurements

Spray drift measurements indicated that dicamba residues were not detected above the no observed adverse effect concentration (NOAEC) for soybeans (2.6x10<sup>-4</sup> lb ae/A, or a deposition fraction of 5.2x10<sup>-4</sup>) in any of the upwind, left wind, or right wind samples during the hour after application. Dicamba was detected at a maximum fraction of the applied deposition of 0.00134194 in downwind samples (Table 1, pp. 56-61), and only exceeded the NOAEC for one other sample (5 m, first hour after application).

To develop the deposition curves for the downwind transects, data were fit to a modified Morgan-Mercer-Floden function, similar to how spray drift deposition estimates were derived for the AgDRIFT, ground application model.

$$f = \frac{1}{(1+ad)^b}$$

where f is the fraction of the application rate at distance d (m). The fitted parameters are a and b, where a is the 'slope' parameter and b is the curvature of the function. Typically, the fitted equation would include a term to account for the deposition from each swath. However, as the path of application was not always perpendicular to the deposition collectors, this term was removed from the equation. The coefficients were obtained by fitting the field data for the various transects.

The reviewer estimated a distance from the edge of the field to reach NOAEC for soybeans  $(2.6 \times 10^{-4})$  lb ae/A, or a deposition fraction of  $5.2 \times 10^{-4}$ ) of 2.8 m (1.3 to 6.0 m for the three transects) in the downwind direction. The study authors did not perform fits of spray drift data,

determining that they would not be useful due to the low levels of dicamba mass detected in the majority of samples (p. 34).

#### D. Plant Effects Measurements

There are concerns with the conduct and conditions of this study. Notably, significant precipitation between planting and application led to ponding in parts of the study area, which resulted in stunted soybeans and areas of low plant population and highly variable plant heights within the test site. Distance to effect estimates for height extend much further than the 10% VSI estimates suggesting that the observed plant height effects are likely consequences of field conditions rather than dicamba exposure.

At 28 DAT, 5% VSI were reported in several volatility transects, only RWA had 10%VSI at 3m from the treated area (**Table 7**). The downwind spray drift (uncovered) transects had significant VSI with distance relationships along several transects. In the DW, RW and SE transects distance to 10%VSI extended out to or beyond 16m (maximum 39 m).

Significant reductions in plant heights were also observed to have distance to effect patterns (i.e., more reduction closer to the treated area) in areas downwind of the treated area (e.g., EE, and NE transects, **Table 7**). Although the study author attempted to minimize variability by selecting plot distances that had plants of similar height at the start of the study, plant height differed across the field due to responses of the condition of the field. Therefore, due to the non-uniformity of plant height across the field, there increased uncertainty in the distance estimates based on a 5% reduction relative to the control growth. The impact of dicamba specific reductions in plant height are confounded by field conditions and differential growth rates across the non-tolerant soybean crop such that reduction of expected plant height (i.e., 5% reduction of mean control height) as a result of dicamba exposure is likely masked by the variable nature of conditions in the field.

Table 8. Estimated distances to regulatory threshold responses for reductions in plant height and visible signs of injury.

Spray Drift + Volatility Volatility **Exposure Pathway** (uncovered transects) (covered transects) Distance to Distance to 10% Distance to 5% Distance to 5% Transect 10% VSI Height (meters) VSI (meters) Height (meters) (meters)  $>90^{b}$  $<3^{b}$  $<3^{\rm b}$  $18.0^{a}$ **DWA** Drift 107.4<sup>a</sup>  $<3^{b}$  $<3^{\rm b}$  $29.6^{a}$ **DWB** Drift 42.7a <3 b <3 b 39.3<sup>b</sup> **DWC** Drift  $\overline{<3^{b}}$ <3 b <3 b <3 b LWA Drift <3 b <3 b LWB Drift <5  $<3^{b}$  $<3^{\rm b}$ <3 b NE Drift NA NA <3 b <3 b NW Drift NA NA <20<sup>b</sup> <3 b RWA Drift 119.7<sup>c</sup> 15.5a 105.7<sup>c</sup>  $16.7^{a}$ <3 b <3 b **RWB** Drift

SE Drift	67.6 <sup>a</sup>	31.5 <sup>a</sup>	NA	NA
SW Drift	>90 <sup>b</sup>	<3 b	NA	NA
UWA Drift	<40 <sup>b</sup>	<3 b	<3 b	<3 b
UWB Drift	<20 <sup>b</sup>	<3 b	<3 b	<3 b

<sup>&</sup>lt;sup>a</sup> distance estimated with logistic regression

NA = Not applicable

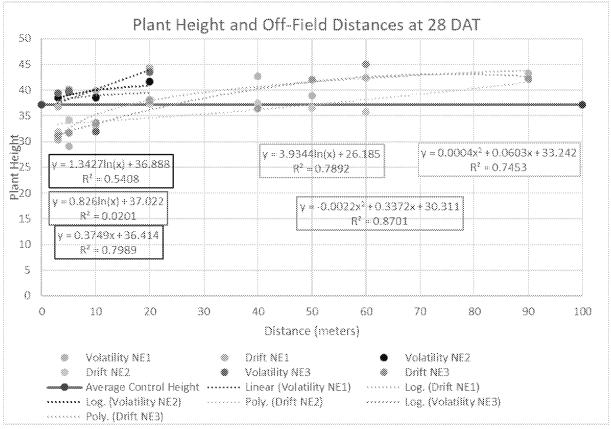


Figure 6: Regression of plant height effects at 28 days after treatment (DAT) and distance from the edge of the treated area for "NE" covered and uncovered transects".

<sup>&</sup>lt;sup>b</sup> distance estimated visually

<sup>&</sup>lt;sup>c</sup> distance estimated with polynomial regression

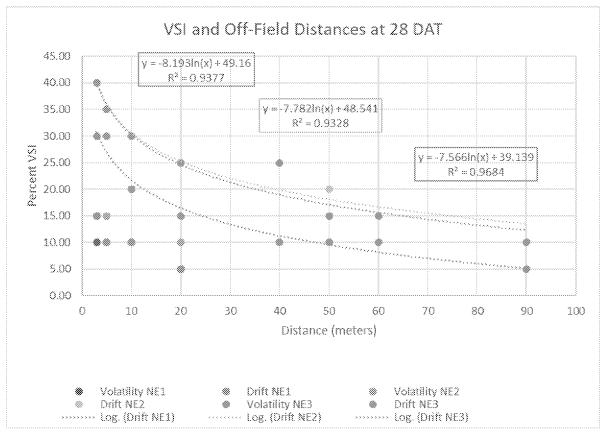


Figure 7: Regression of VSI at 28 days after treatment (DAT) and distance from the edge of the treated area for "NE" covered and uncovered transects".

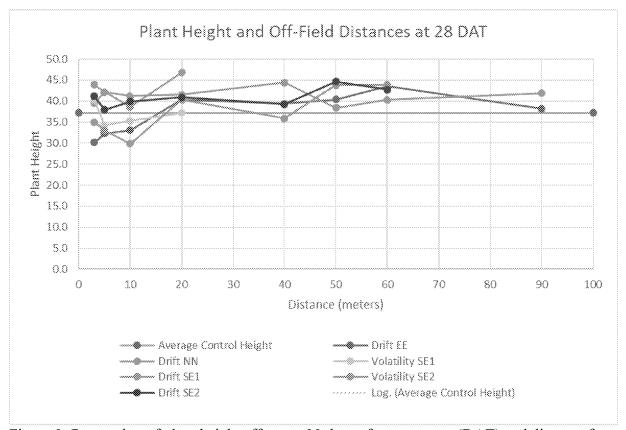


Figure 8: Regression of plant height effects at 28 days after treatment (DAT) and distance from the edge of the treated area for "NN" and "EE" and "SE" uncovered and covered transects.

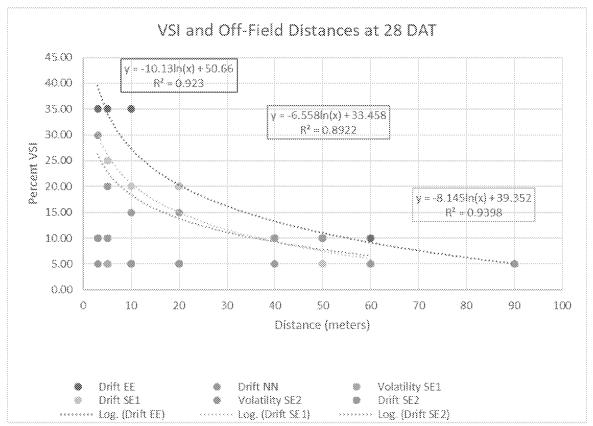


Figure 9: Regression of VSI at 28 days after treatment (DAT) and distance from the edge of the treated area for "NN" and "EE" and "SE" uncovered and covered transects.

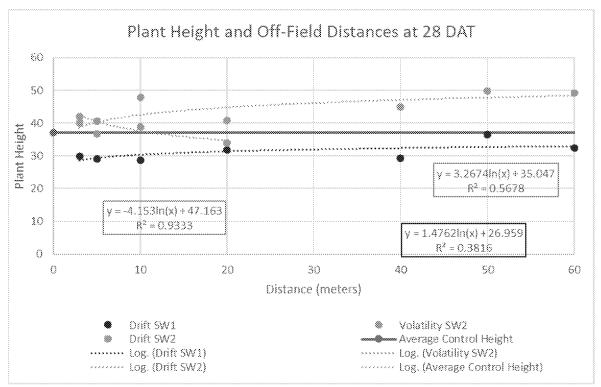


Figure 10: Regression of plant height effects at 28 days after treatment (DAT) and distance from the edge of the treated area for "SW" transects.

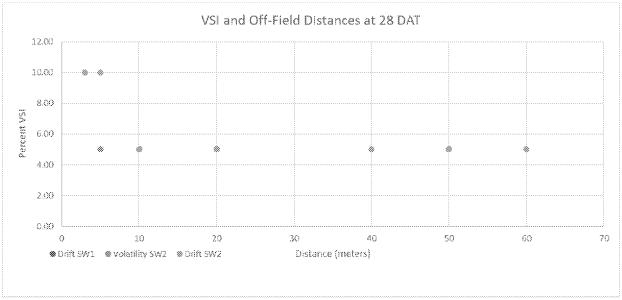


Figure 11: Regression of VSI at 28 days after treatment (DAT) and distance from the edge of the treated area for "SW" transects.

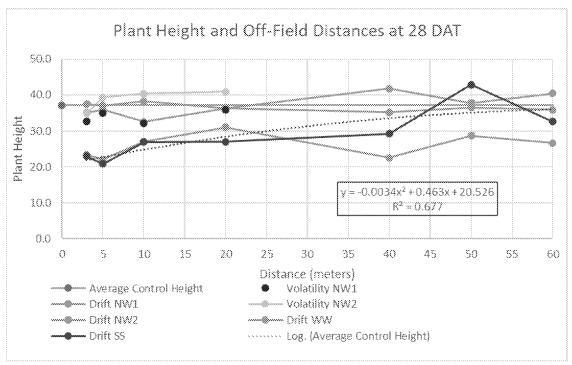


Figure 12: Regression of plant height effects at 28 days after treatment (DAT) and distance from the edge of the treated area for "NW", "WW" and "SS" covered and uncovered transects.

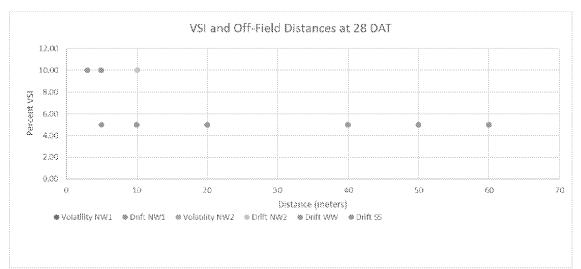


Figure 13: Regression of VSI at 28 days after treatment (DAT) and distance from the edge of the treated area for ""NW", "WW" and "SS" covered and uncovered transects.

## III. Study Deficiencies and Reviewer's Comments

- 1. The surface roughness was typically higher than 0.1, adding uncertainty to the flux rates estimated using the integrated horizontal flux method. Likewise, the fetch distance was typically less than the minimum required for use of the aerodynamic method, adding to the uncertainty of the flux rates estimated using this method.
- 2. The flux calculated for period 7 using the integrated horizontal flux method is inconsistently high relative to fluxes calculated for other periods using the integrated horizontal flux method. The flux is also inconsistent with fluxes calculated for period 7 via the indirect and aerodynamic methods.
- 3. The study was conducted in compliance with U.S. EPA Good Laboratory Practice requirements with exceptions related to statistical analysis, test site information, study weather data, pesticide and crop history, soil information, test plot preparation and maintenance, and sprayer maintenance (p. 3).
- 4. The first air monitoring period started after the conclusion of application.
- 5. Analytical method validation was performed, but the method was not independently validated. A method validation study should be completed from an independent laboratory separate from and prior to the analysis of the test samples to verify the analytical methods.
- 6. Soil was characterized (p. 111 and Appendix I, Table 2, p. 133), but no taxonomic classification was provided.
- 7. Soil bulk density and organic matter content were reported but at only a single depth of 0-6 inches.

#### **Study Deficiencies: Plant Effects**

1. The study author reports the amount of dicamba deposited on filter paper samples during the study period on all transects, distances from the treated area, and sampling times were low in magnitude. The amount of dicamba deposited on filter paper samples during application (filter papers collected in 1 hour after application) had low detections on downwind transects; only two filter paper samples had residue levels that exceeded 0.000522 fraction of applied (at target application rate of 0.5 lb dicamba a.e./A). Filter samples from other transects had residue levels that were also lower than 0.000522 fraction of applied, and many had residue levels between the LOD (0.0015 μg/Filter; equivalent to 0.00000515 fraction of applied) and the LOQ (0.005 μg/Filter; equivalent to 0.00000504 fraction of applied). Many samples had residue levels below the limit of detection (0.0015 μg/filter paper). Due to these low levels of residues, a non-linear regression fit was not performed to the data as originally planned in the protocol (p. 39). The wind rose diagram (Figure 3, p. 80), also shows the wind direction during the first week following application was not predominantly in the downwind direction.

- 2. For both the volatility and spray drift portions of the study, the study author measured the height of a varying number of plants along each transect prior to test material application. Following application, "plants were selected non-systematically with no attempt to measure the same plant at the subsequent time points" (Appendix I, p. 122).
  - OCSPP guidance recommends that the integrity of the replicate should be maintained throughout the duration of the study. In this study, plant height was determined for ten different plants at slightly different distances at each sampling interval. Although the study author reported that 'plants selected for plant height measurements were selected non-systemically as an unbiased representation for the population," the reviewer suggests that this sampling method is inadequate and introduces unnecessary variability into the study results that should have been more systematically controlled.
- 3. For the volatility study, the study author did not determine the significance of differences in soybean height compared to negative control soybean height; therefore, reviewer's results could not be compared to the study authors for the volatility study.
- 4. Transects, except the downwind drift and volatility study transects, totaled 10-20 plants for analysis per distance instead of 30 overall as recommended by OCSPP guidance.
- 5. Transects for spray drift were 60 m long (three upwind sides and two diagonals) and approximately 90 m long (downwind side and the two downwind diagonals) with measurements/symptomology ratings completed at approximately 3, 5, 10, 20, 40, 50, 60, and 90 m from the sprayed area. The study did not report actual distances for each of the height measurements.
- 6. The study author did not provide historical germination rates for the soybean varieties planted.
- 7. The control plot was placed upwind of the treatment field. The specific distance upwind from the edge of the field was not reported.
- 8. The physico-chemical properties of the test material were not reported.
- 9. The 4268FP variety of soybean that was planted in the test plots for both the volatility and spray drift study, is a non-Dicamba tolerant soybean. This variety was also selected because of its glyphosate-tolerance. It is uncertain if this genetically modified variety may have impacted dicamba effects compared to a non-genetically modified variety.

#### IV. References

Johnson, B., Barry, T., and Wofford P. 1999. Workbook for Gaussian Modeling Analysis of Air Concentrations Measurements. State of California, Environmental Protection Agency, Department of Pesticide Regulation. Sacramento, CA.

- Majewski, M.S., Glotfely, D.E., Paw, K.T., and Seiber, J.N. 1990. A field comparison of several methods for measuring pesticide evaporation rates from Soil. Environmental Science and Technology, 24(10):1490-1497.
- Monsanto Method ME-1902-2; Determination of Dicamba in Polyurethane Foam (PUF) Air Sampling Traps by LC MS/MS. 2017.
- Wilson, J.D., and Shum. W.K.N. 1992. A re-examination of the integrated horizontal flux method for estimating volatilisation from circular plots. Agriculture Forest Meteor. Vol 57:281-295.
- Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and Yates, M.V. 1996. Methyl Bromide Emissions from a Covered Field: II. Volatilization," Journal of Environmental Quality, 25: 192-202.

# **Attachment 1: Chemical Names and Structures**

Dicamba-diglycolamine and S-metolachlor and Its Environmental Transformation Products. A

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)	Final %AR (study length)
		PARENT				
Dicamba-diglycolamine (Diglycolamine salt of dicamba)  S-metolachlor	IUPAC: 3,6-Dichloro-o-anisic acid-2-(2-aminoethoxy)ethanol  CAS: 2-(2- Aminoethoxy)ethanol;3,6- dichloro-2-methoxy-benzoic acid  CAS No.: 104040-79-1  Formula: C <sub>12</sub> H <sub>17</sub> Cl <sub>2</sub> NO <sub>5</sub> MW: 326.17 g/mol SMILES: COc1c(Cl)ccc(Cl)c1C(=O)O.NC COCCO  IUPAC: 2-Chloro-N-(6-ethyl-o-tolyl)-N-[(1S)-2-methoxy-1-methylethyl]acetamide  CAS: 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl]acetamide  CAS No.: 87392-12-9  Formula: C <sub>15</sub> H <sub>22</sub> ClNO <sub>2</sub> MW: 283.8 g/mol SMILES: Cc1cccc(CC)c1N(C(=O)CCl)C(C)COCC	H <sub>3</sub> C H <sub>2</sub> CH <sub>3</sub> H <sub>2</sub> CH <sub>3</sub> H <sub>2</sub> CH <sub>3</sub> H <sub>2</sub> CH <sub>3</sub> H <sub>2</sub> CCH <sub>3</sub> H <sub>2</sub> CCH <sub>3</sub> H <sub>2</sub> CCH <sub>3</sub>	835.8100 Field volatility	50958201	NA	NA
	MAJOR (>	>10%) TRANSFORMATION PRODUCTS	S			

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)	Final %AR (study length)			
	No major transformation products were identified.								
	MINOR (	<10%) TRANSFORMATION PRODUCTS	5						
	No minor transformation products were identified.								
REFERENCE COMPOUNDS NOT IDENTIFIED									
All compounds used as reference compounds were identified.									

A AR means "applied radioactivity". MW means "molecular weight". NA means "not applicable".

## **Attachment 2: Statistics Spreadsheets and Graphs**

Supporting spreadsheet files accompany the review.

1. Air sampling periods and soil temperature and moisture graphs



128931\_50958201\_DE R-FATE\_835.8100\_5-14

2. Validation spreadsheet for the Indirect Method



128931\_50958201\_DE R-FATE\_835.8100\_5-14

3. Validation spreadsheet for the Integrated Horizontal Flux Method



128931\_50958201\_DE R-FATE\_835.8100\_5-14

4. Validation spreadsheet for the Aerodynamic Method



128931\_50958201\_DE R-FATE\_835.8100\_5-14

5. Air modeling files



128931 50958201 air modeling.zip

6. Validation spreadsheet for spray drift calculations



128931\_50958201\_DE R-Fate\_840.1200\_8-29

7. Terrestrial Plants: Vegetative Vigor. MRID 50958201, EPA Guideline 850.4150

Folder: 128931 50958201 850.4150

# Attachment 3: Field Volatility Study Design and Plot Map



Figure obtained from Appendix I, Figure 2, p. 170 of the study report.